Author(s): Imamura, N. & Singh, K. & Pelloquin, D. & Simon, Ch. & Sasagawa, T. & Karppinen, Maarit & Yamauchi, H. & Maignan, A.

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Magnetodielectric response of square-coordinated MnO 2 unit in cubic BiMn 7 O 12

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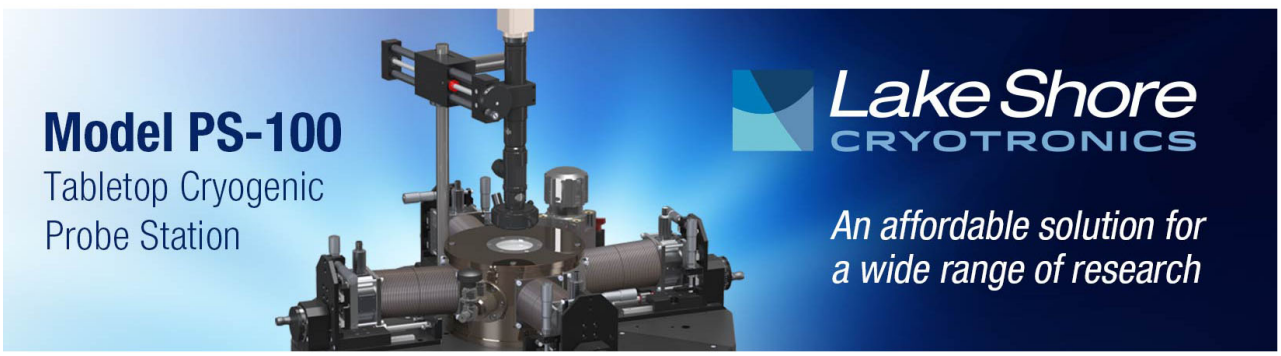

Magnetodielectric response of square-coordinated MnO_2 unit in cubic $BiMn_7O_{12}$

N. Imamura,[1] K. Singh,[1] D. Pelloquin,[1,a)] Ch. Simon,[1] T. Sasagawa,[2] M. Karppinen,[3] H. Yamauchi,[3] and A. Maignan[1]
[1]*Laboratoire CRISMAT, UMR 6508 CNRS-ENSICAEN, 6 Boulevard Maréchal Juin, 14050 Caen Cedex 4, France*
[2]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*
[3]*Department of Chemistry, Laboratory of Inorganic Chemistry, Aalto University, FI-00076 Aalto, Finland*

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The magnetodielectric (MD) effect for $BiMn_7O_{12}$ with the cubic $A'A''_3B_4O_{12}$-type A-site-ordered perovskite structure has been investigated. A clear negative MD response around and beyond T_N has been observed and attributed to antiferromagnetic spin fluctuations. With further decreasing temperature ($T \ll T_N$) a switching to a complex positive MD effect is found confirming additional contribution coming from the magnetic ordering. The present study underlines the importance of square-coordinated $Mn_{A''}O_2$ units for generating MD coupling in an $A'A''_3B_4O_{12}$-type structure; the magnitude of the MD effect then strongly depends on the precise chemical composition. © *2011 American Institute of Physics*. [doi:10.1063/1.3551540]

Materials that show drastic responses to various external stimuli attract considerable attention due to their high technological potentials, or multifunctionality, as well as scientific interest. Strongly coupled multiple degrees of freedom of electron, e.g., spin, charge, and orbital, in the strongly correlated electron systems are expected to lead to unprecedented device applications, e.g., colossal magnetoresistance and spin-driven ferroelectricity in perovskite manganese oxides.[1–3] The so-called magnetodielectric (MD) effect observed in some exotic magnetic insulators/semiconductors is a phenomenon resultant from strongly coupled dielectric-magnetic interactions which provide additional tunability of dielectric constant by means of controlling the external magnetic field.[4] In general the intrinsic MD coupling in a magnetic insulator is large only about the magnetic ordering temperature, while that is subtle in the paramagnetic phase including the geometrically frustrated magnetic state. For practical application larger MD coupling and high controllability by magnetic fields are highly desired. Thus it is necessary to gain deeper understanding and materials design concept of the MD phenomena. In the present study we investigated the MD effect in the A-site-ordered manganese perovskite $(BiMn_3)_A(Mn_4)_BO_{12}$ or $BiMn_7O_{12}$, where Bi^{3+} with the $6s^2$ lone-electron-pair and Mn^{3+} show very unusual ordered arrangement at the A-site of the simple ABO_3 perovskite [see Fig. 1(a); visualized with the software VESTA (Ref. 5)].

Depending on the excess oxygen content, or in other words cation deficiency, $BiMn_7O_{12}$ takes monoclinic $LaMn_7O_{12}$-type and cubic $CaCu_3Ti_4O_{12}$-type structures, both of which consist of the same $Mn_{A''}O_2$ unit.[6–8] Intriguing MD effect was discovered depending on temperature range or magnetic state in monoclinic $BiMn_7O_{12}$ of single-valent Jahn–Teller (JT) system,[6] whereas the relaxation of the JT distortion for the Mn_BO_6 octahedra and the corresponding lack of Mn_B magnetic ordering were found in the more strongly oxygenated phase of cubic $BiMn_7O_{12}$.[7] It has been reported that not only spin fluctuations induced by antiferromagnetic (AFM) ordering and the shift of the magnetic transition temperature caused by external magnetic fields but also magnetic-field-induced spin realignment may contribute to the MD response in monoclinic $BiMn_7O_{12}$.[6] Thus it is interesting to investigate the MD effect in oxygen-rich cubic $BiMn_7O_{12}$ and compare with that in the monoclinic one to gain deeper understanding of the coupled magnetic dielectric properties.

Cubic $BiMn_7O_{12}$ was prepared through high-pressure synthesis as reported previously.[7] Electron diffraction (ED) coupled with energy dispersive spectroscopy (EDS) has been carried out to check the lattice. As illustrated by [100] and

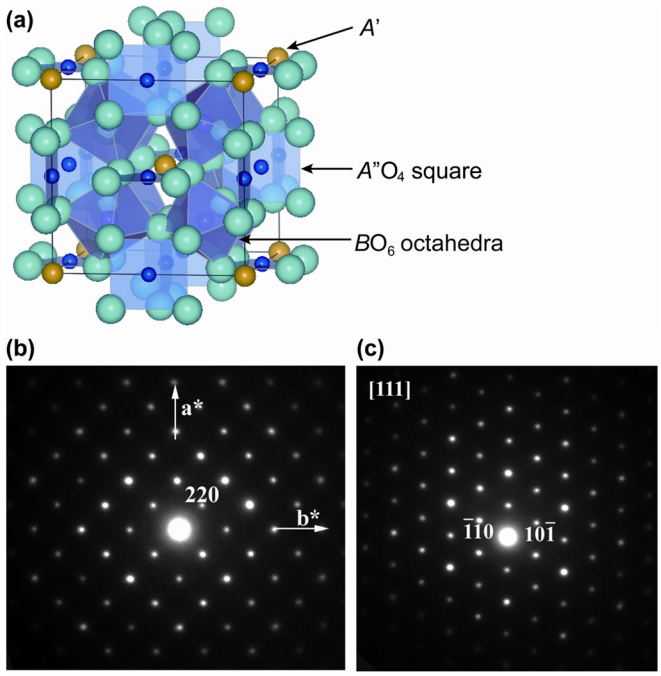

FIG. 1. (Color online) (a) Crystal structure of $A'A''_3B_4O_{12}$. Square-coordinated $A''O_2$ units align perpendicular to each other. Experimental (b) [100] and (c) [111] ED patterns collected in cubic $BiMn_7O_{12}$.

a)Electronic mail: denis.pelloquin@ensicaen.fr.

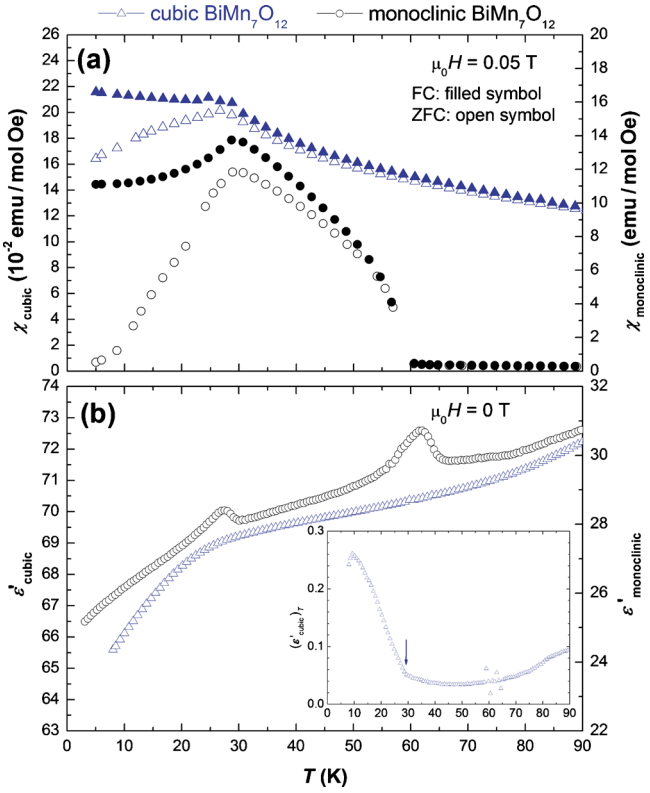

FIG. 2. (Color online) (a) Magnetic susceptibility depending on temperature for cubic and monoclinic $BiMn_7O_{12}$ measured under 0.05 T. (b) Dependence on temperature of real part of relative dielectric constant (ε'; at 100 kHz) under 0 T for cubic and monoclinic $BiMn_7O_{12}$. The inset shows $\partial\varepsilon'/\partial T$ for cubic $BiMn_7O_{12}$ as a function of temperature. The data for monoclinic $BiMn_7O_{12}$ were taken from Ref. 6, for comparison.

[111] ED patterns shown in Figs. 1(b) and 1(c), an hexagonal network is observed along the [111] zone axis, while the [100] ED pattern leads to a cell parameter close to 7.5 Å in agreement with the expected cubic ($2a_p \times 2a_p \times 2a_p$) lattice. Corresponding EDS data reveal a homogeneous average cation composition close to the nominal one. A thin layer of indium was deposited on the opposite parallel surfaces of the polished bulk sample for capacitance measurements. Capacitance and dielectric loss were measured from 8 K to room temperature (rate: 2 K/min) using an Agilent 4248A RLC bridge allied with physical property measurement system (Quantum Design) at different frequencies (1–100 kHz) to ensure that the results are not frequency-dependent and the loss angle is always below 0.2% (not shown here).

Figure 2 shows the temperature dependence of the magnetic susceptibility χ and the dielectric constant ε' for cubic and monoclinic $BiMn_7O_{12}$. We found clear dielectric anomalies associated with the magnetic phase transition(s) for both cubic and monoclinic phases. For cubic $BiMn_7O_{12}$ there is a clear drop in slope around the AFM ordering temperature T_N, which is evidenced in the $\partial\varepsilon'/\partial T$ versus T plot [see the inset of Fig. 2(b)]. In cubic $BiMn_7O_{12}$ the decrease in ε' below T_N indicates the coupling between the polarization and the magnetization, which is related to the AFM ordering, while the smaller change in ε' around T_N suggests a weaker MD coupling.

The effect of external magnetic field H on dielectric property for cubic $BiMn_7O_{12}$ is presented in Fig. 3. The inflection temperature, where ε' decreases sharply, shifts to the lower temperature side with increasing H, as clearly evidenced in the dielectric loss [see Fig. 3(b)]. These findings are compatible with the magnetic susceptibility data,[7] indicating that the AFM transition in cubic $BiMn_7O_{12}$ is very sensitive to H. Accordingly ε' is also strongly affected by H.

To explore the effect of H on ε' in cubic $BiMn_7O_{12}$ we measured the MD ratio $\{\equiv[\varepsilon'(\mu_0H)-\varepsilon'(\mu_0H=0)]/\varepsilon'(\mu_0H=0)\}$ as a function of H at several temperatures, as shown in Fig. 4. It is found that the sign and shape of the MD versus H curve depend on temperature. A symmetric negative MD effect with smooth H-dependence is observed around T_N, being compatible with the expectation for AFM compounds,[9] whereas a positive MD response is as well seen below T_N. These observations are very similar to the case of monoclinic $BiMn_7O_{12}$. A closer look to the MD data collected from 25 to 5 K clearly reveals the existence of a shoulder at a characteristic magnetic field ($H_{flop} \approx 5$ T at 20 K). This H_{flop} value increases with decreasing temperature. The origin of this feature is not clear, and further experiments are required to clarify the feature. In addition, the MD measurements show a negative MD effect just above T_N in the paramagnetic region (see 35 and 50 K data in Fig. 4), which may be due to short-range AFM spin fluctuations. The MD response above T_N does not vary too much with increasing temperature.

The magnitude of the MD ratio is found to be smaller in cubic $BiMn_7O_{12}$ compared to that in monoclinic $BiMn_7O_{12}$,[6] which is consistent with the tiny change in ε' around T_N presented in Fig. 2(b). The negative-to-positive MD switching below T_N clearly suggests the different origin of the MD effect observed around and well below T_N, besides the high-sensitivity of T_N to H. These findings are common in cubic and monoclinic $BiMn_7O_{12}$, and we may thus conclude that the intriguing MD effects in cubic and monoclinic $BiMn_7O_{12}$ are presumably of the same origin.

Important structural features of cubic and monoclinic $BiMn_7O_{12}$ are that (1) the square-coordinated $Mn_{A''}O_2$ unit exists in both the forms, and (2) the monoclinic phase exhibits distorted or JT-active Mn_BO_6 octahedra, whereas regular octahedral coordination is seen for the cubic phase. The rigidity of the lattice is related to how strongly multiple degrees of freedom of electrons are coupled. Hence, from a viewpoint of crystal structure and magnetic behavior, the observed complex MD effects may be caused by the peculiarly ordered square-coordinated $Mn_{A''}O_2$ unit, which induces coupled magnetic and dielectric interactions. The difference in magnitude could be understood by considering the degree of Bi $6s^2$ lone-pair-induced orbital hybridization, which reflects the strength of the chemical bonding and may thus cause different structural features.[10–12] Another possible explanation might be the difference in the rigidity of the lattice through the $Mn_{A''}$-O-Mn_B-O-$Mn_{A''}$ magnetic exchange pathway. Namely, the stronger connection between $Mn_{A''}$ and Mn_B via common O is expected in monoclinic $BiMn_7O_{12}$ with JT-active Mn_BO_6 octahedra than in the JT-inactive cubic form. Superexchange interaction through the A''-O-B-O-A'' path in addition to the direct exchange interaction between the A'' cations is known to play a significant role in the sign and magnitude of the magnetic coupling in $A'A''_3B_4O_{12}$.[10,13] Therefore the $Mn_{A''}$-O-Mn_B-O-$Mn_{A''}$ path in monoclinic $BiMn_7O_{12}$ would play a role not only in global magnetic interactions but also in the MD coupling.

It is worth to mention that similar coupled magnetic-dielectric interactions below T_N have been observed in isos-

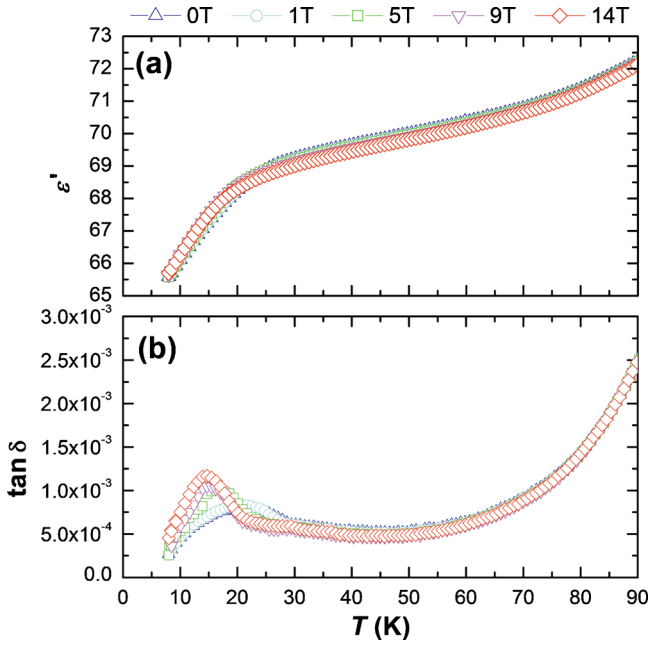

FIG. 3. (Color online) Temperature dependence of (a) dielectric constant ε' and (b) dielectric loss tan δ for cubic $BiMn_7O_{12}$ under various magnetic fields.

tructural $CaCu_3Ti_4O_{12}$, too.[14] Parallel dielectric behaviors below the A''-site magnetic ordering temperature in monoclinic and cubic $BiMn_7O_{12}$ and in $CaCu_3Ti_4O_{12}$ confirm that the $A''O_2$ unit in the $A'A''_3B_4O_{12}$-type compounds is important for the generation of the MD response. In other words, the unusually ordered arrangement of the $A''O_2$ units favors coupled magnetic-dielectric interactions below the A''-site magnetic ordering temperature. The picture of strongly connected crystal and magnetic structures can be valid not only in $CaCu_3Ti_4O_{12}$,[15] but also in many other $A'A''_3B_4O_{12}$-type compounds. The $A'A''_3B_4O_{12}$-type structure is known to be robust against chemical substitution blocked by the square-coordinated $A''O_2$ unit such that the tilting of the BO_6 octahedra is less affected by the A cation size as compared to simple ABO_3 perovskite. Thus, in that structure, the chemical bonding can be easily modified by means of chemical pressure control.[16] Such structural characteristics also play an important role in materials design.

To summarize, a negative-to-positive MD switching and a complex positive MD phenomenon well below T_N in the $A'A''_3B_4O_{12}$-type $BiMn_7O_{12}$ have been evidenced. These observations suggest a common intrinsic MD effect for the A-site-ordered $A'A''_3B_4O_{12}$ perovskites. By controlling the strength of the chemical bonding (orbital hybridization) within both the $A''O_2$ units and the BO_6 octahedra and/or the delicate balance between direct exchange interaction with the A'' cations and superexchange interaction through the

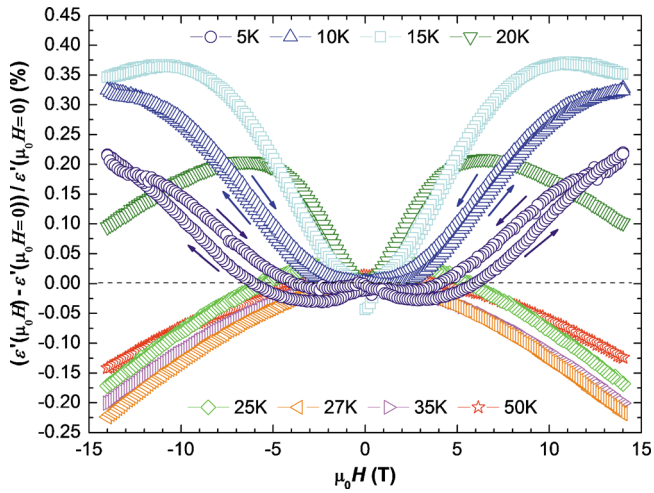

FIG. 4. (Color online) Isothermal magnetic field dependence of the MD ratio $\{\equiv[\varepsilon'(\mu_0 H)-\varepsilon'(\mu_0 H=0)]/\varepsilon'(\mu_0 H=0)\}$ for cubic $BiMn_7O_{12}$ at several temperatures.

A''-O-B-O-A'' path, the $A'A''_3B_4O_{12}$-type system appears to be a very promising family to generate MD devices.

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